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Structure and dynamic properties of substituted carbonylhydride clusters $H_2RuOs_3(CO)_{13}$ and $H_4Ru_4(CO)_{12}$ containing functionalized phosphines

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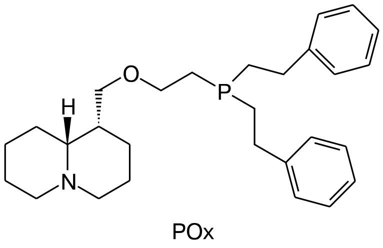
The derivatives of the $H_2RuOs_3(CO)_{13}$ and $H_4Ru_4(CO)_{12}$ carbonylhydride clusters containing functionalized (including chiral) phosphines were synthesized. The solid-state structure of $H_2RuOs_3(CO)_{12}(Ph_2P(C_4H_3S))$ was determined by X-ray diffraction analysis. The structures of other compounds in solution were determined using IR and ^1H and ^{31}P NMR spectroscopy. A study of the temperature dependences of the ^1H NMR spectra of the phosphine-substituted tetrahedral clusters along with the analysis of literature data for their analogs showed that compounds of this type exist in solution as an equilibrium mixture of isomers, which differ in arrangement of the hydride ligands at the cluster skeleton. Interconversion of the isomeric forms is due to migration of the hydride ligands over the cluster skeleton. A general model for this dynamic process was proposed. The model is consistent with both our data and earlier results of other authors.

Key words: carbonylhydride clusters, transition metals, chiral ligands, functionalized phosphines, synthesis, structure, dynamic properties.

Carbonylhydride clusters of the iron subgroup transition metals are used as efficient catalysts in hydrogenation of unsaturated organic compounds.[1—4] From this point of view, it seems most attractive to consider phosphine-substituted derivatives of the $H_4Ru_4(CO)_{12}$ and $H_2RuOs_3(CO)_{12}$ clusters, whose activity in various organic reactions is well known.[1—14] Reactions of asymmetric synthesis[15] are especially interesting from the theoretical and applied viewpoints, and reactions of this type catalyzed by cluster compounds have been most poorly studied up to date, and only restricted examples of using the clusters in asymmetrical catalysis are available in the literature.[16—18]

As a rule, in the organometallic complexes of this type the hydride ligands participate in the low-barrier dynamic processes, such as hydride migration over the cluster skeleton in solution[19—24] and even in the solid phase.[25—27] The fast intramolecular hydride exchange in the cluster compounds in solution has been evidenced for the first time for a series of compounds $H_4Ru_4(CO)_{12-x}L_x$ ($L = P(OMe_3)$, $x = 1—4$).[28] However, subsequent more detailed studies[22,29] of the structure of the ligand environment and mechanism of dynamic processes in these compounds revealed no general pattern, and some conclusions of the above cited works even contradict each other.

In this work, we synthesized new tetrahedral monosubstituted carbonylhydride clusters with functionalized phosphine ligands $H_2RuOs_3(CO)_{12}(PS)$ (**1**) and $H_4Ru_4(CO)_{11}L$ (**2—5**), where L = POx (**2**), PSug (**3**), PInd (**4**), and PStyr (**5**); PS is thienyldiphenylphosphine, POx is (1*R*,9*R*)[2(oxymethylquinolisidinyl)ethyl]di(2-phenylethyl)phosphine, PSug is (2-[5-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl]oxyethyl)di(2-phenylethyl)phosphine, PInd is [2-(1-indolyl)propyl]di(2-phenylethyl)phosphine, PStyr is (2-phenylpropyl)distyrylphosphine. The structures of compounds **1—5** in solution were studied, and a model for the dynamic behavior of their coordination sphere was proposed.



POx

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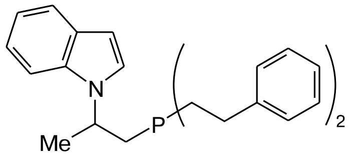
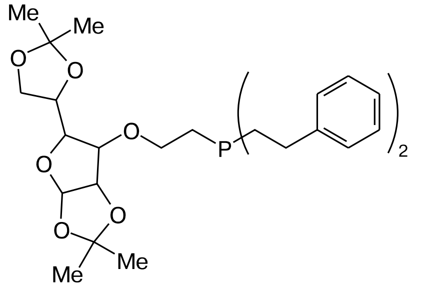


PInd



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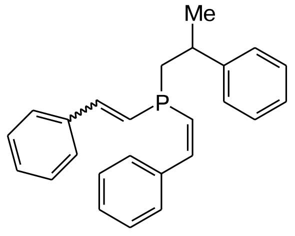


PStyr

Experimental

IR spectra were recorded on a Specord M-80 instrument in CH_2Cl_2. ^1H and ^{31}P NMR spectra were measured on a Bruker DX 300 instrument in $CDCl_3$. The mass spectrum of cluster **1** was obtained on a JEOL MS 700T instrument (ESI+). The mass spectra of clusters **2—5** were obtained on a Trio 2000 instrument (FAB+) using 3-nitrobenzyl alcohol as the matrix. The isotope distribution in the spectra of molecular ions and their fragments corresponds completely to the theoretically calculated set of signals, which is a convincing evidence for the proposed composition of the synthesized compounds. Dichloromethane, chloroform, hexane, methanol, and ethanol (Vekton Ltd., Russia) were used as solvents; hexane, methanol, and ethanol were used as received, and the chlorinated solvents were purified using standard procedures. The $H_4Ru_4(CO)_{12}$ [30] and $H_2RuOs_3(CO)_{13}$ [31] clusters and functionalized phosphines, *viz.*, PS,[32] POx,[33] PSug,[34] PInd,[35] and PStyr,[36] were synthesized according to earlier published procedures. $Me_3NO \cdot 2H_2O$ (Aldrich) was sublimed *in vacuo* prior to use.

Cluster $H_2RuOs_3(CO)_{12}(PS)$ (1). A solution of the $H_2RuOs_3(CO)_{13}$ cluster (112 mg, 0.11 mmol) and $Ph_2P(C_4H_3S)$ (PS) (28 mg, 0.11 mmol) in chloroform (20 mL) was refluxed for 2 h in a round-bottom flask with a reflux condenser. The reaction course was monitored by TLC. Target product **1** was isolated by column chromatography using a hexane—diethyl ether (5 : 1, v/v) mixture as eluent. The yield was 95 mg (69%). MS (ESI+), *m/z*: $C_{28}H_{15}O_{12}Os_3PRuS$ 1278 $[M]^+$. IR, ν/cm^{-1}: 2092 m, 2064 vs, 2052 vs, 2036 s, 2028 s, 2008 m, 1996 m, 1836 w. br (CO). ^1H NMR, δ, isomer **A**: 7.18—7.25 (m, 1 H); 7.41—7.58 (m, 11 H); 7.69—7.81 (m, 1 H); −19.32 (d, 2 H, J = 7.3 Hz); isomer **B**: −19.69, −21.15 (both br. s, 1 H each). $^{31}P\{^1H\}$ NMR, δ: isomer **A**: 20.0 (m, $^2J^{trans}{}_{Os-P}$ = 46.4 Hz, $^2J^{cis}{}_{Os-P}$ = 11.0 Hz); isomer **B**: 38.7 (m, $^2J^{trans}{}_{Os-P}$ = 51.1 Hz, $^2J^{cis}{}_{Os-P}$ = 11.0 Hz).

Clusters $H_4Ru_4(CO)_{11}L$ (L = POx (2), PSug (3), PInd (4), and PStyr (5)). A solution of phosphine (1 molar equiv.) was syringed into a Schlenk tube contained a deaerated suspension of $H_4Ru_4(CO)_{12}$ (100 mg, 0.134 mmol) in chloroform (5 mL). The reaction mixture was frozen with liquid nitrogen, and a solution of $Me_3NO \cdot 2H_2O$ (30 mg, 0.268 mmol) in chloroform (1 mL) was added dropwise in an argon flow. The tube was then evacuated with an oil vacuum pump and left to warm to ~20 °C under vigorous stirring of the starting $H_4Ru_4(CO)_{12}$. The solution turned intense dark orange. The reaction mixture was separated by column chromatography using as eluents dichloromethane—methanol (10 : 1, v/v) for **2**, dichloromethane—hexane (10 : 1) for **3**, and hexane—dichloromethane (5 : 1) for **4** and **5**. Four bands were obtained (in the order of elution): a broad yellow band of the starting cluster, narrow pale yellow and broad brown bands containing a minor amount of unidentified products, and a broad orange (or yellow-orange) band of the target product. All synthesized compounds are oily uncrystallizable samples that did not allow determination of their elemental composition and exact yield, which was estimated to be ~50%.

Cluster **2**. IR, ν/cm^{-1}: 2084 w, 2052 vs, 2028 s, 2004 m, 1988 w.sh, 1956 w.br (C≡O). ^1H NMR, δ: −17.58 (s, 4 H); 1.40—2.00 (m, 11 H); 2.34 (m, 10 H); 2.90 (m, 7 H); 3.41—4.05 (m, 4 H); 7.15—7.43 (m, 10 H). $^{31}P\{^1H\}$ NMR, δ: 27.7 (s). MS (FAB+), *m/z*: $C_{40}H_{46}NO_{12}PRu_4$ 1168 $[M]^+$, 1140 $[M - CO]^+$, 1112 $[M - 2\ CO]^+$, 1084 $[M - 3\ CO]^+$, 1056 $[M - 4\ CO]^+$, 1028 $[M - 5\ CO]^+$, 1000 $[M - 6\ CO]^+$.

Cluster **3**. IR, ν/cm^{-1}: 2086 w, 2054 vs, 2026 s, 2006 m, 1986 w.sh, 1956 w.br (C≡O). ^1H NMR, δ: −17.56 (s, 4 H); 1.21, 1.39, 1.53 (all s, 3 H each); 2.38 (m, 6 H); 2.92 (m, 4 H); 3.88—4.10 (m, 6 H); 4.53, 4.80 (both d, 1 H, J = 3.5 Hz); 7.18—7.43 (m, 10 H). $^{31}P\{^1H\}$, NMR, δ: 25.7 (s). MS (FAB+), *m/z*: $C_{41}H_{45}O_{17}PRu_4$ 1244 $[M]^+$, 1216 $[M - CO]^+$, 1160 $[M - 3\ CO]^+$, 1132 $[M - 4\ CO]^+$, 1104 $[M - 5\ CO]^+$.

Cluster **4**. IR, ν/cm^{-1}: 2088 w, 2056 vs, 2028 s, 2008 m, 1988 m.sh, 1960 w.br (C≡O). ^1H NMR, δ: −17.54 (s, 4 H); 1.68 (d, 3 H, J = 6.5 Hz); 1.85, 2.60, 2.11, 2.64 (all m, 8 H); 2.43, 3.03 (both m, 2 H); 4.91 (m, 1 H); 6.54—7.75 (m, 16 H). $^{31}P\{^1H\}$ NMR, δ: 28.0 (s). MS (FAB+), *m/z*: $C_{38}H_{34}NO_{11}PRu_4$ 1118 $[M]^+$, 1090 $[M - CO]^+$, 1034 $[M - 3\ CO]^+$, 1006 $[M - 4\ CO]^+$, 978 $[M - 5\ CO]^+$, 950 $[M - 6\ CO]^+$, 922 $[M - 7\ CO]^+$, 894 $[M - 8\ CO]^+$.

Cluster **5**. IR, ν/cm^{-1}: 2092 w, 2084 w, 2052 v.s, 2028 s, 2004 m, 1986 w.sh, 1956 w.sh (C≡O). ^1H NMR, δ: −17.48 (s, 4 H); 1.27 (d, 3 H, Me, J = 6.8 Hz); 2.51 (t, 2 H, J = 6.0 Hz); 3.09 (m, 1 H); 5.56 (dd, 1 H, J = 19.7 Hz, J = 13.7 Hz); 5.95 (dd, 1 H, J = 15.8 Hz, J = 13.7 Hz); 6.69 (dd, 1 H, J = 18.0 Hz, J = 13.7 Hz); 7.00—7.48 (m, 16 H). $^{31}P\{^1H\}$ NMR, δ: 3.7 (c). MS (FAB+), *m/z*: $C_{36}H_{29}O_{11}PRu_4$ 1074 $[M]^+$.

The crystals of compound **1** suitable for X-ray diffraction analysis were grown from a heptane—dichloromethane (5 : 1) mixture at +5 °C. The crystal data, experimental conditions, and structure refinement details are listed in Table 1. The crystals were studied on a Rigaku/MSC Mercury CCD single-crys-

Table 1. Crystallographic data for cluster **1**

Parameter	Value
Molecular formula	$C_{28}H_{13}O_{12}Os_3PRuS$
Formula weight	1276.11
Temperature/K	293
λ/Å	0.71070
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell parameters	
a/Å	24.891(1)
b/Å	14.1941(8)
c/Å	9.2388(5)
V/Å^3	3264.1(3)
Z	4
d_{calc}/g cm^{-3}	2.597
μ(Mo-Kα)/cm^{-1}	122.60
$2\theta_{max}$/deg	55.0
Number of collected/unique reflections	24672/3756
R_{int}	0.066
$R_1{}^a$ ($I \geq 2\sigma(I)$)	0.031
$wR_2{}^b$ ($I \geq 2\sigma(I)$)	0.075

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. [b] $wR_2 = \{\Sigma[w(F_0{}^2 - F_c{}^2)^2]/\Sigma[w(F_0{}^2)^2]\}^{1/2}$.

tal diffractometer at the Osaka-City University. The data were collected and processed using the Crystal Clear program (Rigaku). Absorption correction was applied. The structure was solved by a direct method,[37] and missing atoms were found by the difference Fourier synthesis.[38] Positions of non-hydrogen atoms were refined in the anisotropic approximation.[39] All calculations were performed using the teXsan[40] crystallographic software package of Molecular Structure Corporation.

Results and Discussion

Synthesis, structure, and dynamic behavior of the hydride ligands in the $H_2RuOs_3(CO)_{12}(PS)$ cluster (1). Heating of a mixture of $H_2RuOs_3(CO)_{13}$ and $Ph_2P(C_4H_3S)$ (PS) in chloroform gives the monosubstituted cluster $H_2RuOs_3(CO)_{12}(PS)$ (**1**) in high yield. The isotopic distribution of the molecular ion in the mass spectrum of compound **1** corresponds to that calculated for $C_{28}H_{15}O_{12}Os_3PRuS$. The IR spectrum in the region of carbonyl vibrations contains absorption bands of the terminal and μ_2-bridging carbonyl groups. The ^{1}H NMR spectrum in the aromatic region exhibits a set of multiplets typical of the terminally (through the phosphorus atom) coordinated ligand.[41] The molecular structure of compound **1** determined by the X-ray diffraction method is shown in Fig. 1, and selected bond lengths and bond angles are given in Table 2. The cluster molecule is a tetrahedron of three osmium atoms and one ruthenium atom, which is surrounded by the ligand shell of ten terminal and two semibridging CO groups, one phosphine, and two hydride ligands. Sixty valence electrons in cluster **1** correspond to the closed tetrahedral configuration of the cluster skeleton.[42] Potentially bidentate[41,43] thienyldiphenylphosphine is coordinated with the Ru(1) atom through the phosphorus atom only, and the thienyl group of the ligand is not involved in coordination and remains free. Each of the Os(2) and Os(3) atoms are bound to three terminal CO groups, whereas Ru(1) and Os(1) coordinates two terminal CO ligands each. Two CO ligands are coordinated in a semibridging mode over the Os(1)—Os(3) and Os(1)—Os(2) bonds, which is indicated by Os(1)—C(4)—O(4) and Os(1)—C(6)—O(6) bond angles values of 158.1(1) and 159.2(1)°, respectively, and the Os(2)—C(4) (2.52(1) Å) and Os(3)—C(6) (2.55(1) Å) distances, which are about ~0.9 Å shorter than the nonbonding Os—C(O) contacts for other terminal carbonyl ligands in cluster **1**.

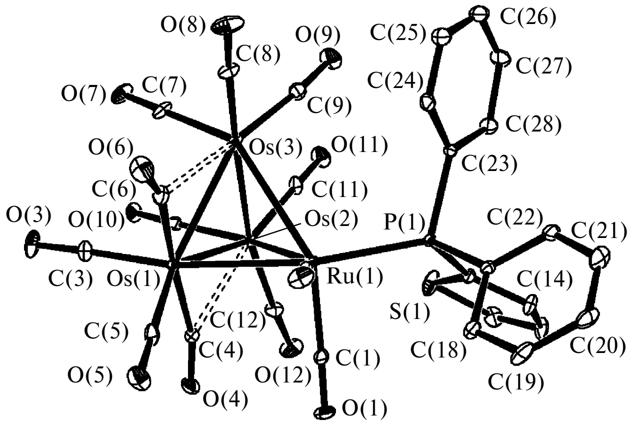


Fig. 1. Molecular structure of cluster **1**.

A possible arrangement of two hydride ligands in structure **1** can be suggested on the basis of well documented trends concerning relative metal—metal (M—M) bond lengths for the carbonylhydride clusters. In these com-

Table 2. Selected structural parameters of cluster **1**

Parameter	Value	Parameter	Value
Bond	d/Å	Bond	d/Å
Ru(1)—Os(1)	2.7963(6)	Os(3)—C(7)	1.92(1)
Ru(1)—Os(2)	2.9635(6)	Os(3)—C(8)	1.92(1)
Ru(1)—Os(3)	2.9697(6)	Os(3)—C(9)	1.89(1)
Os(1)—Os(2)	2.8072(5)	Os(2)—C(10)	1.93(1)
Os(1)—Os(3)	2.8129(4)	Os(2)—C(11)	1.88(1)
Os(2)—Os(3)	2.8283(5)	Os(2)—C(12)	1.91(1)
Ru(1)—P(1)	2.360(2)	Os(3)—C(6)	2.55(1)
Ru(1)—C(1)	1.894(10)		
Ru(1)—C(2)	1.905(9)	Angle	ω/deg
Os(1)—C(3)	1.91(1)	P(1)—Ru(1)—Os(1)	168.37(6)
Os(1)—C(4)	1.95(1)	P(1)—Ru(1)—Os(2)	113.09(5)
Os(1)—C(5)	1.91(1)	P(1)—Ru(1)—Os(3)	110.98(5)
Os(1)—C(6)	1.98(1)	Os(1)—C(4)—O(4)	158.1(1)
Os(2)—C(4)	2.52(1)	Os(1)—C(6)—O(6)	159.2(1)

plexes, the M—M bonds at which the bridging hydrides are localized are by ~0.2 Å longer than other M—M bonds, including those at which the bridging carbonyl groups are located.[**17,24,44—49**] An analysis of the M—M distances in structure **1** (see Table 2) suggests with a high degree of probability that the hydride ligands in the solid state are coordinated in bridging mode over the Ru(1)—Os(2) and Ru(1)—Os(3) edges in the *cis*-position with respect to the phosphorus atom of the phosphine ligand.

The $^{31}P\{^{1}H\}$ NMR spectrum of cluster **1** at −50 °C displays two singlets at δ 38.9 and 19.9 with the intensity ratio 1.3 : 1. This indicates that cluster **1** exists in solution as two forms with different structures of the ligand shell containing coordinated phosphine. The rise of temperature to 50 °C does not change the general appearance of the spectrum but the ratio of integral intensities changes to 1 : 1. The observed changes are reversible and indicate that the solution contains two isomeric equilibrium forms of cluster **1**. The signals detected in the $^{31}P\{^{1}H\}$ NMR spectrum of cluster **1** display characteristic satellites due to the interaction with the ^{187}Os nuclei: isomer **A** with δ 20.0 ($^{2}J_{Os-P}$ = 46.4 (1.5%) and 11.0 (3.0%) Hz) and isomer **B** with δ 38.7 ($^{2}J_{Os-P}$ = 51.1 (1.5%) and 11.0 (3.0%) Hz) (the integral intensities of the satellite components with respect to the major signal are given in parentheses). The typical one-bond P···Os spin-spin coupling constants are 260—280 Hz[**50**] that makes it possible to assign the observed signals to the structures in which the phosphine ligand is coordinated to the ruthenium atom. The presence of two pairs of satellites at each signal is due to two-bond osmium—phosphorus coupling, namely, with the osmium atoms of the Os_3 triangle, namely, with two *cis* ($^{2}J^{cis}_{Os-P}$ = 11.0 Hz) and one *trans* ($^{2}J^{trans}_{Os-P}$ = 51.1 and 46.4 Hz) osmium atoms of the Os_3 triangle. The relative intensities of the components of the satellites are completely consistent with the proposed structure. Thus, the $PRuOs_3$ fragment of cluster **1** has the same structure in solution as that found in the solid state, and the presence of the isomers can be due to the different arrangement of the hydride ligands at the tetrahedral metal skeleton.

The limiting low-temperature ^{1}H NMR spectrum of cluster **1** (−50 °C) contains three main signals located at δ −19.48 (d, J_{P-H} = 9.2 Hz), −19.76 (s), and −21.21 (d, J_{P-H} = 9.2 Hz) and relative integral intensities of 10 : 7 : 7, respectively. This spectroscopic pattern can be explained by the presence in solution of isomeric forms **A** (δ −19.48) and **B** (δ −19.76 and −21.21), whose integral intensities of the signals agree completely with the ^{31}P NMR spectroscopy data. Selective decoupling of the interaction with the corresponding phosphorus nuclei confirmed the P—H-nature of the observed spin-spin coupling, the values of spins-spin coupling constants being consistent with the $^{2}J^{cis}_{P-H}$ values found earlier[**46,51**] for the carbonylhydride clusters of the iron subgroup. These data suggest structural models shown in Fig. 2 for isomers **A** and **B**. In the structure of isomer **A**, both hydrides are equivalent and occupy the *cis*-position relative to the phosphine that completely corresponds to the obtained spectral data. In isomer **B**, hydrides are inequivalent and one of them occupies the *cis*-position with respect to the phosphine, to give the doublet at δ −21.21. The singlet signal (δ −19.76) of the second hydride of this isomeric form does not display spin-spin coupling with the other hydride ligand either in 1D, or in the ^{1}H COSY NMR spectra. Thus, this ligand can occupy a bridging position only at one of the edges of the Os_3 triangle that is verified by the characteristic satellites in the ^{1}H NMR spectrum ($^{1}J_{Os-H}$ = 30.2 Hz). The absence of coupling with another hydride leaves for this ligand a unique position shown in Fig. 2.

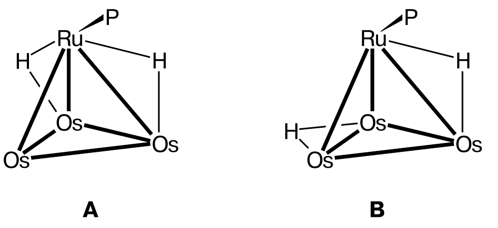


Fig. 2. Scheme of the mutual disposition of the phosphine and hydride ligands on the tetrahedral metal skeleton of cluster **1** for isomers **A** and **B**.

Gradual broadening of the signals corresponding to form **B** observed with the temperature rise in the hydride part of the ^{1}H NMR spectrum of cluster **1**. The broadening is accompanied by a decrease in the integral intensity of these signals compared to that of the hydrides of isomer **A** and by disappearance of the fine structure of the doublet at δ −21.21 (Fig. 3). At +25 °C the signal at δ −21.21 is transformed into a broad singlet ($\Delta_{1/2}$ = 27 Hz), whereas at 45 °C both signals of the hydrides of form **B**

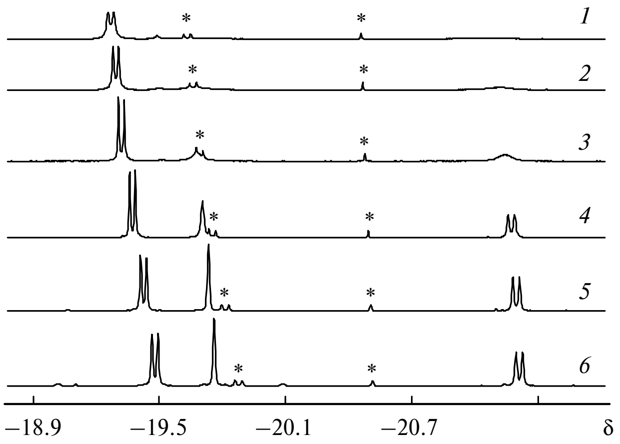
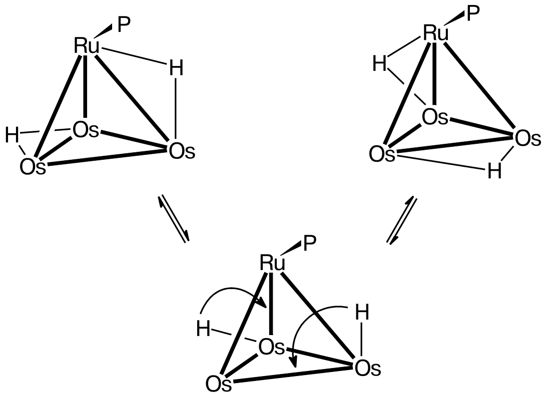


Fig. 3. ^{1}H NMR spectra ($CDCl_3$) of cluster **1** at 45 (*1*), 35 (*2*), 25 (*3*), 0 (*4*), −25 (*5*), and −50 °C (*6*). The signals of admixtures are marked with asterisks.

degrade into baseline. The hydride signal of form **A** remains nearly unchanged in the temperature interval from −50 to 35 °C. The changes observed in this temperature range are due to the intramolecular exchange of the hydrides in form **B** and show no transformations of the isomeric species into each other. The most probable mechanism of exchange is a concerted migration of the hydrides over the cluster skeleton as shown in Scheme 1. In the absence of basic distinctions in structure of the isomers, it seems rather evident that in form **A** the hydride ligands also participate in the analogous intramolecular dynamic process, which does not change the line shape of this hydride signal, because the exchanging hydrides are equivalent. Only at 45 °C the equilibrium of $\mathbf{A} \rightleftarrows \mathbf{B}$ isomerization results in broadening for the hydride **A** signal.

Scheme 1



It is of interest to compare the data on the structures and dynamic behavior of cluster **1** synthesized in the present work and the earlier[45] studied triphenylphosphine-substituted analog $H_2RuOs_3(CO)_{12}(PPh_3)$, which was obtained as crystals of two types. In one of them, the phosphine ligand is coordinated to the ruthenium atom, and in the second one to the osmium atom of the tetrahedral metal skeleton. The authors failed to separate the isomers chromatographically, and all spectral data presented were attributed to a mixture of forms coexisting in solution. The spectral characteristics of this mixture, according to the results of $^{31}P\{^1H\}$ (δ 49.39 (s), 33.60 (s)) and ^1H (hydride region, δ −19.51 (d, J_{P-H} = 7.4 Hz), −19.74 (s), −21.29 (d, (J_{P-H} = 9.1 Hz)) NMR spectroscopy, are completely analogous (relative position and multiplicity of signals) to the data obtained for cluster **1**. The authors[45] claimed that the forms of the cluster with phosphine coordination at the ruthenium and osmium atoms, which were found upon crystallization of the compound, should be considered as isomers in this system. The fast dynamic process observed in the ^1H NMR spectrum at room temperature is the phosphine transfer between the osmium and ruthenium atoms. Interpretation of this kind seems feasible for several reasons. First, no data were presented[45] on the Os—P and Os—H spin-spin coupling constants, which could indicate unambiguously the coordination mode of the phosphine and hydrides relative to the osmium atoms of the metal skeleton. In addition, actual processes of a phosphine ligand migration between adjacent atoms of the cluster skeleton were observed for the very restricted number of systems[51,52] at temperatures much higher than ambient temperature that is evidently dictated by high strength of the metal—phosphorus bond and instability of the bridging forms of phosphine coordination. Therefore, the most probable explanation for the behavior of the $H_2RuOs_3(CO)_{12}(PPh_3)$ cluster in solution can be given by the structural and dynamic models proposed by us for cluster **1**, and crystallization of the isomer with the phosphine ligand coordinated with the osmium atom is due, most likely, to the low solubility of this minor (admixture) form.

Structure and dynamic behavior of the $H_4Ru_4(CO)_{11}L$ clusters (2—5) in solution. The $H_4Ru_4(CO)_{12}$ cluster reacts with functionalized phosphines under mild conditions in the presence of trimethylamine *N*-oxide to form $H_4Ru_4(CO)_{11}L$, where L = POx (**2**), PSug (**3**), PInd (**4**), and PStyr (**5**), as the major product. The synthesized compounds form no crystalline phases and, therefore, their compositions and structures were determined by the data of mass spectrometry, IR and NMR spectroscopy. The mass spectra of all isolated compounds contain signals from molecular ions and fragmentation products [$M^+ - n$CO]. All the signals demonstrate the characteristic isotope distribution corresponding to the elemental composition of the respective ions. The IR spectra of clusters **2—5** in the region of carbonyl ligand vibrations are almost identical and contain absorption bands of the terminal carbonyl groups only. The positions and relative intensities of the absorption bands of clusters **2—5** in this region correspond, with high accuracy, to the parameters of the IR spectra of the monosubstituted $H_4Ru_4(CO)_{11}L$ clusters characterized (including crystallographic methods) earlier.[29,53,54] This match suggests that compounds **2—5** are monosubstituted derivatives of the $H_4Ru_4(CO)_{12}$ cluster in which the phosphine ligand occupies one of the terminal positions in the coordination sphere of the cluster and the structure of the carbonyl environment does not differ from that for the already known $H_4Ru_4(CO)_{11}L$ clusters. The $^{31}P\{^1H\}$ NMR spectra of clusters **2—5** at room temperature contain one singlet signal each. The singlet signal exhibits a considerable downfield shift compared to the signals of free phosphines that indicates in favor of heteroligand coordination onto the cluster core through the phosphorus atom. The organic part of the ^1H NMR spectra of these compounds contains signals of protons corresponding by the number and very close in chemical shifts and multiplicity to the spectral characteristics of the free ligands. These data confirm monodentate coordination of the phosphines through the phosphorus atom only, despite the presence of organic substituents containing other coordinating functional groups, such as the double bond in the styryl radical of the PStyr cluster, the nitrogen(III) atoms in the PInd and POx clusters, and the ether oxygen atoms in the PSug and POx clusters. Obviously, this is caused by rather bulky substituents at the coordinating functions in the PInd, POx, and PSug clusters. The double bond of styryl-substituted phosphine in the PStyr cluster is not coordinated because, most likely, of mismatch between the bite angle of the potentially bidentate ligand and the bridging or terminal vacancies available for coordination on the Ru_4 metal skeleton.

At room temperature the hydride region of the ^{1}H NMR spectra of clusters **2—5** contains only one broaden signal with integral intensity corresponding to four hydride ligands. This is indicative of the fast exchange process involving all hydride ligands. The study of the temperature dependences of the ^{1}H NMR spectra of all the four compounds in the temperature interval from 25 to −95 °C showed almost identical changes in the number and line shape of the hydride signals. This points to the same structure of the coordination sphere of clusters **2—5** in solution and similar dynamic behavior of the hydride ligands. The typical temperature dependence of the ^{1}H NMR spectra of the monosubstituted clusters is shown in Fig. 4 for compound **2** as an example. When the temperature decreases to −70 °C, the signal observed at ambient temperature is split into two broad signals with equal intensities, which appear at −95 °C as comparatively narrow doublets at −16.50 ($^2J_{P-H}$ = 29.6 Hz), a singlet at δ −16.71, and a doublet at δ −18.77 ($^2J_{P-H}$ = 10.7 Hz) (relative integral intensities 1 : 1 : 2), and two broad signals at δ −17.0 and −18.3 (integral intensities 1 : 1). As a whole, the ratio of integral intensities of the first and second groups is ~1 : 2. The presence of two groups of signals in the low-temperature spectrum can be explained by the presence in solution of at least two isomeric cluster forms different in arrangement of hydrides on the metal skeleton.

In the first group of well resolved signals the upfield (δ −18.77 (2 H, J = 10.7 Hz)) and downfield (δ −16.50 (1 H, J = 29.6 Hz)) doublets can be assigned to hydrides located in the *cis*- and *trans*-positions, respectively, with respect to phosphine judging from the values of spin-spin coupling constant. The singlet signal of the relative intensity 1 is attributed, most likely, to the hydride remote from the phosphine at a distance longer than two bonds. The structure corresponding to this scheme of spin-spin coupling is shown in Fig. 5 (structure **A**). This structure has been determined earlier[29] in the crystalline phase of the $H_4Ru_4(CO)_{11}(PMe_2Ph)$ cluster. Analogous arrangement of hydrides on the Ru_4 metal skeleton is typical of disubstituted derivatives of the cluster containing bridging phosphines[17,46,48,49] and, hence, the obtained spectral data can reasonably be assigned just to structure **A**.

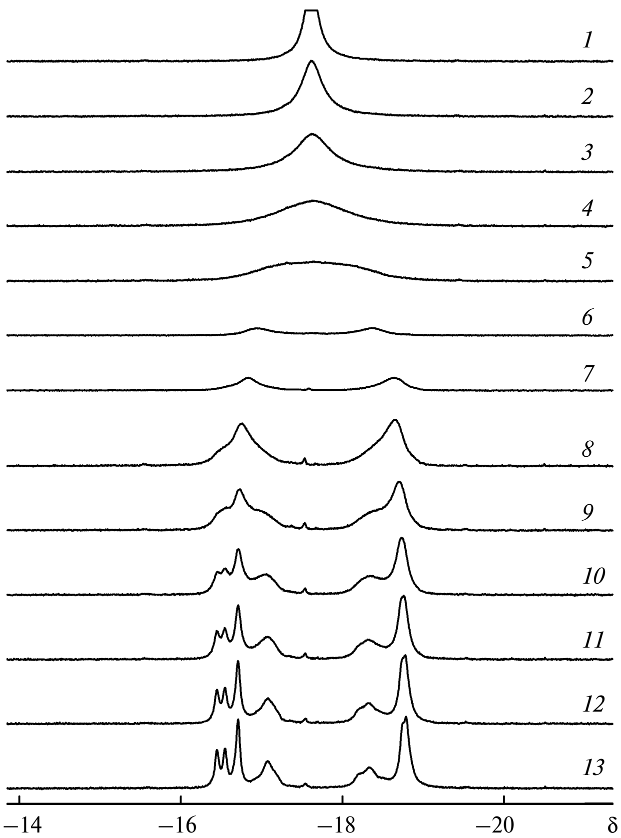


Fig. 4. ^{1}H NMR spectra (CD_2Cl_2) of cluster **2** at 0 (*1*), −5 (*2*), −10 (*3*), −15 (*4*), −20 (*5*), −30 (*6*), −70 (*7*), −80 (*8*), −83 (*9*), −86 (*10*), −89 (*11*), −92 (*12*), and −93 °C (*13*).

The second set of broaden signals at δ −17.1 and −18.3 corresponds to the isomeric form in which hydride exchange is not completely frozen, and it is difficult to draw certain conclusions about the structure of this isomer from the spectral characteristics of cluster **2**. However, in this case, it is helpful to compare the data obtained in this work with the characteristics of the monosubstituted ana-

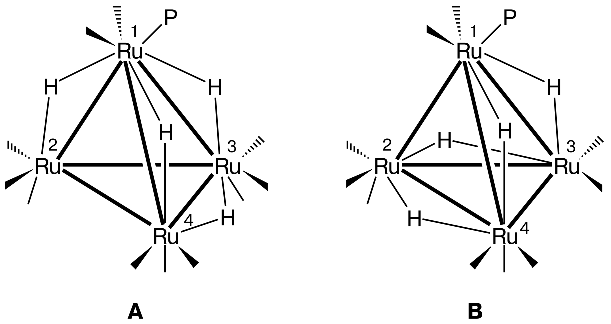


Fig. 5. Structures of isomeric forms **A** and **B** for the $H_4Ru_4(CO)_{11}PR_3$ clusters.

logs $H_4Ru_4(CO)_{11}L$ (L = $P(C_6F_5)_3$, $P(OMe)_3$, PMe_2Ph,[29] PPh_3, and $P(OEt)_3$ (see Ref. 22). The low-temperature limiting spectra of the $P(OEt)_3$ [22] and PMe_2Ph [29] substituted clusters are shown in Fig. 6. The spectra of both compounds are similar and resemble much the spectrum of cluster **2**. The both spectra contain a set of two downfield signals (doublet and singlet) and one upfield (doublet) signal with the relative intensity 1 : 1 : 2. The spin-spin coupling constant of the downfield signal is higher by several times than that of the downfield signal that fits completely to the spectral characteristics of cluster **2**. The spectra of these clusters also exhibit two signals of equal intensity corresponding to another form (isomer) of these compounds. In the spectrum of $H_4Ru_4(CO)_{11}PMe_2Ph$ (see Ref. 29) at –90 °C, the signals of this form (marked as D_{2d} (see Fig. 6)) are considerably broadened due to the fast exchange process similar to the spectrum of cluster **2**, this form being the minor one. In the spectrum of $H_4Ru_4(CO)_{11}P(OEt)_3$ [22] (–120 °C), the signals mentioned above appear as two singlets or slightly broaden multiplets but, unlike the PMe_2Ph derivative, this isomer is the major one. In the above cited articles,[22,29] these signals are reasonably ascribed to symmetrical structure **B** (see Fig. 5), as it has been done for cluster **2**. However, the second set of resolved signals is interpreted as a combination of signals from several (two[22] or even three[29]) isomers, which exist in equilibrium and differ in phosphine disposition relative to the tetrahedron edges occupied by hydrides and free of these ligands. This assignment seems very doubtful, because for all the compounds under study the relative intensities of signals are constant, being 1 : 1 : 2. This invariability can hardly be expected for several equilibrated forms of so different phosphine-substituted clusters, especially taking into account the difference in relative concentrations of isomer **B** in these systems. Therefore, the most probable hypothesis, which makes it possible to describe the ^1H NMR spectra of these hydride clusters from the general viewpoint, is the assignment of the first set of signals as a combination of the singlet (1 H), doublet (1 H, high $^{31}P-^1H$ spin-spin coupling constant), and doublet (2 H, low $^{31}P-^1H$ spin-spin coupling constant) generated by isomer **A** (see Fig. 5).

The thorough analysis of the temperature dependence of the ^1H NMR spectra of synthesized cluster **2** (see Fig. 4) shows that in the temperature interval from –95 to –70 °C the main dynamic process is the $\mathbf{A} \rightleftarrows \mathbf{B}$ isomerization, because the resulting chemical shifts of broadened signals at δ –16.8 and –17.6 are weighed average values for the downfield and upfield signals of these two forms. Similar spectral changes are also observed in the temperature dependence (–(120—90) °C) of the ^1H NMR spectrum of the $H_4Ru_4(CO)_{11}P(OEt)_3$ cluster.[22] This dynamic process can be described in terms of concerted migration of the bridging hydrides in isomer **A** from the Ru(1)—Ru(2) and Ru(3)—Ru(4) edges to positions at the Ru(2)—Ru(3) and Ru(2)—Ru(4) edges, whereas two other hydrides do not physically migrate over the metal skeleton. The concerted exchange of this type is a low-barrier process that explains its emergence at so low temperatures. Upon the further temperature increase, the spectra of all monosubstituted derivatives under study display the collapse of the hydride signals, indicating the complete intramolecular exchange of all the hydride ligands. Thus, the present study in combination with the analysis of available literature data made it possible to develop a general model for the structure of isomeric forms of the $H_4Ru_4(CO)_{11}PR_3$ clusters and dynamics of the hydride ligands in the coordination sphere of these compounds.

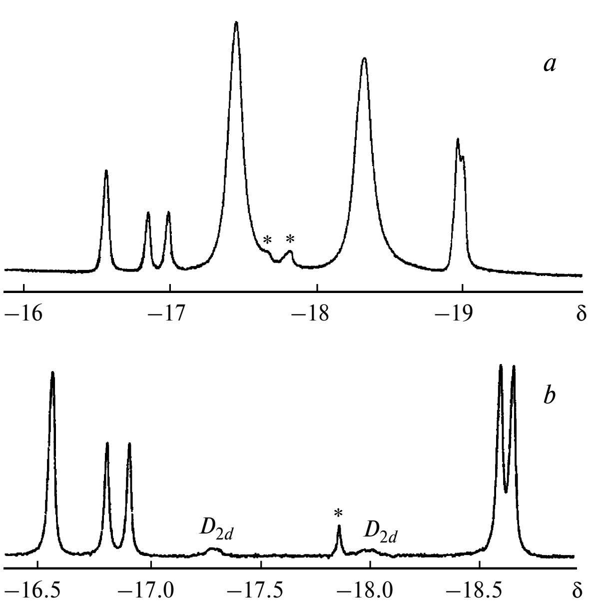


Fig. 6. ^1H NMR spectra of the $H_4Ru_4(CO)_{11}(P(OEt)_3)$[22] (*a*) and $H_4Ru_4(CO)_{11}(PMe_2Ph)$[29] (*b*) clusters in the hydride region. The signals of admixture are marked with asterisks. Symbol D_{2d} was used[29] to designate signals of isomers assigned to the corresponding point symmetry group.

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